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## **Predicting the growth of graphene nanostructures using high-fidelity atomistic simulations**

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**Final report of LDRD project #165698:**

**Predicting growth of graphene nanostructures  
using high-fidelity atomistic simulations**

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**Abstract**

In this project we developed the atomistic models needed to predict how graphene grows when carbon is deposited on metal and semiconductor surfaces. We first calculated energies of many carbon configurations using first principles electronic structure calculations and then used these energies to construct an empirical bond order potentials that enables comprehensive molecular dynamics simulation of growth. We validated our approach by comparing our predictions to experiments of graphene growth on Ir, Cu and Ge. The robustness of our understanding of graphene growth will enable high quality graphene to be grown on novel substrates which will expand the number of potential types of graphene electronic devices.

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## NOMENCLATURE

CVD	Chemical Vapor Deposition
DFT	Density Functional Theory
MD	Molecular Dynamics
vdW	van der Waals

## 1. INTRODUCTION

Graphene continues to attract widespread attention due to its outstanding electronic and optical properties for next-generation electronics. In future applications, device functionality critically depends on producing graphene nanomaterials with high quality and uniformity (with few or no defects). Inserting these novel electronic materials into real world devices requires discovering improved understanding to better control growth. Among the numerous methods for graphene synthesis, chemical vapor deposition (CVD) growth on transition metal substrates stands out for producing large-area films amenable to commercial applications.

In particular, large-area graphene growth on copper (Cu) foils (the most commonly used substrate) shows the greatest promise because low solubility of carbon in Cu inherently favors single-layer graphene growth. However, despite its potential, the detailed mechanisms or conditions for controlled graphene growth are unknown or very poorly characterized, often leading to a wide variety of nanostructures. Specifically, how graphene grows on different Cu facets, what controls its in-plane orientation, and how intrinsic Cu defects affect nucleation and defect formation remain inadequately understood. Indeed, even how graphene is aligned, in terms of its crystallography, with Cu itself remains an open question. Consequently, it is extremely difficult to design experimental procedures that will lead to reproducible, controlled growth of optimal nanostructures. A theoretical understanding of the detailed mechanisms of graphene growth is needed to help tailor the experimental conditions to generate high-quality graphene nanostructures. The aims of this project were to: 1) develop a paradigm-changing computational capability for predicting the growth of graphene nanostructures on a metallic substrate, 2) validate the capability through comparison to experimental observations of graphene growth on Cu, and 3) use this predictive tool to understand the fundamental mechanistic processes and conditions (temperature, pressure, deposition rate, and substrate orientation) that govern high-quality growth, and 4) perform a proof-of-concept demonstration to down-select a subset of candidate growth experiments for graphene nanostructures to be carried out under specific conditions.

## 2. ACCOMPLISHMENTS

The principal results of this project have been published in six journal articles [1-6]. Rather than repeat the content of these papers, in the following we present to the reader a commentary about how these published papers address the goals of the project.

Previous experimental work has established that graphene growth does not occur by the simple attachment of single carbon atoms [7]. Instead it involves a complex series of events that involve as many as five atoms. Our strategy to understanding and predicting this process is to perform long time scale molecular dynamics (MD) simulations. To do this we needed to develop empirical potentials that can be evaluated with little computational effort, but describe both the carbon-carbon bonding and the carbon-substrate bonding. This is challenging because of the completely different character of these two interactions. To overcome this difficulty we used the bond order potential formalism. We used density functional theory (DFT), to calibrate the C-C potential. This work is described in Ref. [1].

The validity of this potential was verified by successfully performing simulations of graphitic- and diamond-like carbon. Combined with previously determined potentials for substrate interactions (such as for Cu [8]), this enables the simulations of growth we have performed.

The interaction of graphene with a substrate, because of its inherent 2-D nature, is quite weak – determined mostly van der Waals (vdW) interactions that are on the order of 100meV/atom. But to minimize defects in graphene films one desires to have graphene epitaxially aligned with the substrate. (Otherwise defects are created when misaligned graphene domains merge.) Thus, a crucial question in modeling vdW epitaxy and predicting graphene quality is whether this interaction is strong enough to allow epitaxy to occur. The answer to this question is uncertain because in DFT, vdW interactions are usually treated in a somewhat ad hoc manner. To put the theory on a firmer basis we performed experiments to determine graphene energies on Ir as a function of in-plane graphene orientations. We find these energies compare well with estimates derived from our vdW DFT calculations. Further, we developed a way of parameterizing the orientation dependence of the vdW interaction with only two easily computed parameters. This work is described in Ref. [2].

Another check of whether the vdW interaction with the substrate is described correctly in our model is that it reproduce measured substrate-graphene distances. To do this we provided experimental electron reflectivity data to collaborators at Carnegie Mellon University who had developed ways of using such data to extract Cu-graphene distances. We found distances in accord with vdW DFT, adding further support to our understanding of vdW epitaxy. This work is reported in Ref. [3].

One of the most important questions about carbon atom attachment to graphene edges is how the attachment process depends on the local structure of the graphene edge. A signature of this dependence is given by the shape of growing graphene crystals. Circular crystals indicate little local dependence on edge structure, while highly facets crystals indicate a strong dependence. In Ref. [4] we report observations that establish that the shape of graphene crystals grown on Ir(111) depends on the orientation of graphene with respect to the substrate. This indicates that the attachment process depends on both on the configuration of the graphene edge and how this configuration is positioned relative to the substrate. A model and explanation of this effect is also described in Ref. [4].

To test our model of how graphene orientations are selected based on the orientation dependence of the vdW interaction, we compared our model to experimental observations of graphene grown on Ge(111) and Ge(110). Previous predictions had explained the better epitaxial alignment on Ge(110) as due to the effect of adsorbed H [9]. We find however, as reported in [5], that our model explains the preference given only the known structures of the clean surface.

Finally, a concern of models which focus on the role of the attachment of elemental carbon to graphene is that they neglect the role of other chemical components of the system. While on metal surfaces, H (from hydrocarbon feedstocks) by itself is unlikely to significantly adsorbed at the high temperature, it is possible that O could be. As part of a large collaboration we established O does indeed have an effect on graphene growth on Cu(001) and proposed models for why this is the case [6].



### **3. CONCLUSIONS**

To enable the creation of higher quality graphene for novel electronics applications, we have developed a MD simulation tool that can predict graphene growth quality on metal surfaces. We have performed extensive molecular dynamics of graphene growth from deposited carbon atoms and have validated our understanding by comparing our predictions to experiments of graphene growth on Ir, Cu and Ge.

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